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<b>(54) Title:</b> IMPROVED STYRENIC RESIN MOLDING COMPOSITION AND FOAM			
<b>(57) Abstract</b>  An optionally rubber-reinforced, monovinylidene aromatic polymer resin composition comprising: a) an optionally rubber-reinforced matrix polymer; and b) a plasticizing amount of a solid (at room temperature and pressure), low molecular weight, polymer of limonene or alpha-methylstyrene and, optionally, another copolymerizable vinyl aromatic monomer, having a weight average molecular weight of from 1,000 to 70,000, a volatiles content of up to 30 percent and a glass-transition temperature of at least about 25 °C. The composition surprisingly has improved flow characteristics, and no substantial decrease in toughness and rigidity. The invention further includes a process for producing a closed-cell polymer foam from the composition of the invention, an expandable or foamable monovinylidene aromatic polymer formulation comprising the composition of the invention and a blowing agent, and the resulting polymer foam. Advantageously, the foam of the invention can be produced using only CO <sub>2</sub> as a blowing agent.			

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## IMPROVED STYRENIC RESIN MOLDING COMPOSITION AND FOAM

The present invention relates to optionally rubber-reinforced styrenic polymers and to a polymeric foam, particularly a styrenic foam.

5 Styrenic molding polymers are useful for preparing molded articles such as small appliances, toys, video cassettes and housings for electronic equipment such as televisions. For these applications, it is highly desirable to have a resin with good flow properties to facilitate the high speed production of complex molded articles. It is also important to have a resin with good physical properties such as rigidity, as expressed by flexural or tensile properties. For most applications, long-term load bearing properties are required. These properties are known to be related to parameters such as flexural stress and flexural modulus for polystyrene, and tensile yield stress, tensile modulus and impact strength for high impact polystyrene. In these molding applications it is also desirable to employ resins with good thermal properties. The resins should be capable of sustaining their load bearing characteristics even at elevated temperatures.

The physical properties of styrene polymers generally improve as the molecular weight of the polymers increases. For resins used in injection molding, the processability of the resin generally decreases as the molecular weight increases beyond a certain point. Accordingly, the choice of molding resins having sufficient properties involves a compromise between physical property requirements and processing requirements. Such compromises will limit the molecular weight range, and hence the physical property range, for a given polymer.

It is common practice to improve the processability of styrenic molding resins by using plasticizers which generally are low molecular weight organic compounds which are miscible with the polymer matrix and give improved processability. Dioctyl phthalate, and other aromatic esters, are commonly employed as plasticizers in acrylonitrile butadiene styrene terpolymers (ABS). White mineral oil is commonly used as a plasticizer for styrene polymers. The use of mineral oil generally improves the flow properties of a molding resin, but leads to deterioration of other properties such as rigidity, toughness, and the heat distortion temperature.

30 U.S. Patent 4,826,919 discloses blends of polyphenylene ether resin, rubber-modified alkenyl aromatic resin, and copolymers of styrene and alpha-methylstyrene having a weight average molecular weight of less than 5,000. The compositions optionally contain a thermoplastic elastomer. The copolymer is employed in an amount which improves the melt flow rate of the blend of polyphenylene ether and rubber-modified alkenyl aromatic resin. The copolymer additive is said to offer greater melt flow improvement compared to higher molecular weight styrenic homopolymers or copolymers. However, the effect is demonstrated only for bromine-containing compositions, and the effect of the bromine on the melt flow behavior is not mentioned.

Thermoplastic foams such as styrenic polymer foams, are widely used in the fields of construction, civil engineering and thermal insulation. The styrenic polymer foam suitable for such applications desirably is extruded and has good dimensional stability and relatively small cells. These foams are the so-called extruded foams. Extruded foams are also employed  
5 in the so-called decorative field wherein a foam plank may be cut into a decorative foam and be used as is or used as a base for further decorative material. For a considerable period of time, styrenic polymer foams have been extruded employing a variety of organic blowing agents, such as chlorofluorocarbons (CFC's), hydrochlorofluorocarbons (HCFC's) and other halogenated hydrocarbons as well as mixtures thereof. However, large efforts currently are  
10 being made to replace CFC's, and other fully halogenated hydrocarbons with more environmentally acceptable blowing agents due to increased environmental concerns about ozone depletion, greenhouse effects and air quality in general.

In view of the deficiencies of known styrenic resin compositions and foams, it would be highly desirable to have a styrenic molding resin having increased flow properties  
15 while having comparable physical properties such as rigidity, toughness, and heat distortion temperature.

Further, it would be desirable to provide a process for preparing a low density styrenic polymer foam using a partially or entirely pristine, that is, nonhalogenated, blowing agent. Furthermore, it also would be highly desirable to provide a low density styrenic polymer  
20 foam, prepared using a partially or entirely pristine blowing agent, with improved processability without sacrificing other physical properties such as compressive strength and dimensional stability.

The molding resin composition of the present invention is such an improved monovinylidene aromatic polymer resin composition comprising: a) an optionally rubber-reinforced monovinylidene aromatic polymer; and b) a plasticizing amount of a low molecular  
25 weight polymer of limonene or alpha-methylstyrene and, optionally, another copolymerizable monomer, the low molecular weight polymer having a weight average molecular weight of from 1,000 to 70,000, a volatiles content of up to 30 percent and a glass-transition temperature of at least about 25°C. The composition surprisingly has improved flow characteristics without  
30 having a substantial decrease in toughness and rigidity. In its non-rubber-reinforced form, the composition surprisingly is as clear as normal (that is, not rubber-reinforced) polystyrene. The composition of the present invention can be used in the preparation of molded articles, such as toys, small appliances, video cassettes, and housings for electronic equipment.

The invention further includes a process for producing a closed-cell polymer foam  
35 from the resin composition of the invention, the resulting polymer foam, and an expandable or foamable monovinylidene aromatic polymer formulation comprising the composition of the invention and a blowing agent. Advantageously, the foam of the invention can be produced using only CO<sub>2</sub> as a blowing agent.

The plasticizer of the present invention serves to improve the flow properties of the host polymer while maintaining or only slightly lowering rigidity and toughness while, surprisingly, maintaining or only slightly lowering the heat distortion temperature.

Advantageously, the plasticizer is a solid at room temperature and pressure, and is a low molecular weight polymer of alpha-methylstyrene or limonene, with d-limonene being the preferred limonene. The plasticizer can be a copolymer or a homopolymer. Advantageously, the plasticizer has a weight average molecular weight of at least 1,000, preferably at least 1,200, more preferably at least 1,500, and most preferably greater than or equal to 5,000. Advantageously the plasticizer has a molecular weight of less than about 70,000, preferably less than about 50,000, more preferably less than about 30,000, and most preferably less than about 25,000.

Advantageously, the Tg of the plasticizer is at least about 25°C. The plasticizers based on the copolymers of alpha-methylstyrene preferably have a glass-transition temperature of at least about 30°C. More preferably, the Tg of the plasticizer is at least about 50°C and most preferably is at least about 70°C. The volatiles content of the plasticizer advantageously is lower than about 30 percent otherwise an excessive drop in the heat properties of the final blend can be expected. Preferably, the volatiles content is less than about 25 percent, and more preferably is less than about 20 percent. For the purposes of the present invention, the volatiles content is measured at 200°C and 2 mm Hg vacuum for 100 minutes.

The plasticizer is employed in a plasticizing amount. Suitably, the amount is such that the melt flow properties of the composition are improved while the toughness and rigidity of the composition are also maintained or only slightly reduced. Advantageously, from 0.1 to 30 weight percent of the plasticizer is employed based on the total weight of the matrix polymer, the plasticizer, and the optional rubbery polymer. Preferably, the plasticizer is employed in an amount which is from 1 to 25 weight percent. More preferably, the amount of plasticizer is from 2 to 20 weight percent, and most preferably the amount is from a 2.5 to 15 percent. Mixtures of plasticizers of the invention can be employed. Advantageously, the polymeric plasticizer is compatible with the monovinylidene aromatic polymer matrix and has a significantly lower viscosity.

The low molecular weight polymer plasticizer can be prepared by any of the known polymerization methods known to those skilled in the art including, for example, anionic, cationic or free radical polymerization. Additionally, many such polymers are commercially available. When a comonomer is employed in the preparation of the plasticizer, the amount of comonomer suitably is less than 50 percent and preferably is less than 20 percent based on the total weight of residual monomer units in the plasticizer. Examples of other comonomers for the plasticizer include, for example, styrene, which is preferred, and the

monomers and comonomers described hereinbelow as being useful in the preparation of the monovinylidene aromatic polymer resin.

The optionally rubber-reinforced monovinylidene aromatic polymer resins are well-known to those skilled in the art, are widely available commercially, and can be prepared by any of the several polymerization methods known to those skilled in the art including, for example anionic, cationic or free radical, which is preferred, polymerization. The rubber-modified polymers can be prepared by well-known methods including, for example, mass, emulsion, suspension and mass suspension methods. Mass polymerization is preferred. In general, continuous methods are employed for polymerizing the monovinyl aromatic compound. The weight average molecular weight of the monovinylidene aromatic polymer resin employed in the present invention advantageously is at least about 100,000 and preferably is at least about 130,000. The weight average molecular weight of the monovinylidene aromatic polymer resin advantageously is less than about 700,000, and preferably is less than about 400,000.

The optionally rubber-reinforced polymer resins of the present invention are derived from one or more monovinyl aromatic compounds. Representative monovinyl aromatic compounds include styrene; alkyl substituted styrenes such as alpha-alkyl-styrenes (for example, alpha-methylstyrene and alpha-ethylstyrene) and ring alkylated styrenes and isomers thereof (for example, ortho ethyl styrene, 2,4-dimethyl styrene and vinyltoluene, particularly; ortho or para vinyl toluene); ring substituted halo-styrenes such as chloro-styrene and 2,4-dichloro-styrene; and styrenes substituted with both a halo and alkyl group such as 2-chloro-4-methylstyrene; and vinyl anthracene. In general, the preferred monovinyl aromatic monomers are styrene, alpha-methylstyrene, one or more of the vinyl toluene isomers, and/or mixture of two or more of these, with styrene being the most preferred monovinyl aromatic compound.

The monomer mixture may optionally comprise minor amounts of one or more additional comonomers, preferably in an amount less than 10 percent by weight of the polymerizable monomer mixture. Suitable comonomers are unsaturated nitriles, for example acrylonitrile; alkyl acrylates and alkyl methacrylates, for example methyl methacrylate or n-butylacrylate; ethylenically unsaturated carboxylic acid monomers; and ethylenically unsaturated carboxylic acid derivative monomers including anhydrides and amides such as maleic anhydride, and maleimides such as N-phenyl maleimide.

The rubbers preferably employed in the rubber-modified resins are those polymers and copolymers which exhibit a second order transition temperature which is not higher than 0°C, preferably not higher than -20°C, and more preferably not higher than -40°C as determined or approximated using conventional techniques, for example, ASTM Test Method D-746-52 T.

Highly preferred rubbers are alkadiene polymers. Suitable alkadienes are 1,3-conjugated dienes such as butadiene, isoprene, chloroprene or piperylene. Most preferred are homopolymers (excepting any coupling monomers) prepared from 1,3-conjugated dienes, with such homopolymers of 1,3-butadiene being especially preferred. Alkadiene copolymer  
5 rubbers containing small amounts, for example less than 15, preferably less than 10 weight percent, of other monomers such as monovinyl aromatics can also be employed.

As used herein, the particle size is the diameter of the rubber particles as measured in the resultant product, including all occlusions of matrix polymer within rubber particles, which occlusions are generally present in the disperse rubber particles of a rubber-  
10 reinforced polymer prepared using mass polymerization techniques. Rubber particle morphologies, sizes and distributions may be determined using conventional techniques such as (for larger particles) using a Coulter Counter (Coulter Counter is a trademark of Coulter Electronics) or, particularly for smaller particles, transmission electron microscopy.

The rubber is advantageously employed in amounts such that the rubber-  
15 reinforced polymer product contains from 2 to 20 percent, preferably from 3 to 17 percent, more preferably 3 to 15 weight percent rubber or rubber equivalent.

The term "rubber" or "rubber equivalent" as used herein to indicate weight amounts of rubber material is intended to mean, for a rubber homopolymer (such as polybutadiene), simply the amount of rubber, and for a block copolymer, the amount of the  
20 copolymer made up from monomer(s) which, when homopolymerized form a rubbery polymer. For example, for calculating the amount of rubber in a composition where a butadiene-styrene block copolymer rubber has been employed, the "rubber" or "rubber equivalent" of the composition is calculated based on only the butadiene component in the block copolymer. Obviously where physical properties or other aspects of the rubber material are measured, the  
25 complete rubber material including any comonomers is referred to.

The monovinylidene aromatic polymer resin can also contain other additives such as additional plasticizers or lubricants such as mineral oil, butyl stearate or dioctyl phthalate; stabilizers, including antioxidants (for example, alkylated phenols such as di-tert-butyl-p-cresol or phosphites such as trisnonyl phenyl phosphite); mold release agents, for example, zinc  
30 stearate; flame retardants and pigments. The compositions of the invention advantageously are substantially free of polyphenylene oxide.

The compositions of the present invention can be prepared by mixing the plasticizer and the styrenic resin using polymer compounding methods well known to those skilled in the art including, for example, dry blending and extrusion. The compositions of the  
35 invention advantageously exhibit improved melt flow properties while essentially maintaining other important physical properties such as rigidity, toughness, heat distortion temperature, and, in the case of clear matrix polymers, transparency.

The compositions of the present invention advantageously can be employed in the preparation of styrenic polymer foam. Some advantages of using the composition of the present invention in a process to prepare foam include: reduced pressure drop across the extrusion line; lower foam density; and maintenance of good mechanical and heat resistance properties of the foam.

The foam blowing method of the present invention comprises foaming a mixture of the styrenic resin of the invention and a blowing agent to produce a styrenic foam. In a preferred embodiment of the method of the invention, the method comprises producing a styrenic foam by heating the styrenic resin in an extruder to produce a molten resin; introducing into the molten resin a blowing agent to produce a plasticized extrusion mass under a pressure sufficient to prevent foaming of the extrusion mass; and extruding the extrusion mass through a die into a zone having a temperature and pressure sufficient to permit foaming of the extrusion mass to produce the styrenic foam.

The blowing agent, that is, foaming agent, used herein can be any known in the art for thermoplastic foams. See, for example, U.S. Patents 3,770,666; 4,311,636; 4,636,527; 4,438,224; 3,420,786; and 4,421,866. Examples of such blowing agents include commonly used liquid or gaseous organic compounds which do not dissolve the polymer and which have a boiling point below the softening point of the polymer. A wide variety of volatile fluid blowing agents which are carbon-containing compounds can be utilized. They include such materials as the aliphatic or cycloaliphatic hydrocarbons including ethane, ethylene, propane, propylene, butane, butylene, isobutane, pentane, neopentane, isopentane, hexane, heptane, cyclohexane and mixtures thereof, as well as fully or partially halogenated hydrocarbons such as methylene chloride, chlorodifluoromethane; 1-chloro-1,1-difluoroethane; 1,1,1,2-tetrafluoroethane; 2-chloro-1,1,1,2-tetrafluoroethane, pentafluoroethane, 2,1,1,1-dichlorodifluoroethane, 1,1-difluoroethane and 1,1,1-trifluoroethane and 1,1-difluoroethane. Preferably, the blowing agents generally exhibit a boiling point of not greater than 100°C at 100 kPa absolute pressure. Other useful fluid blowing agents are the tetraalkyl silanes such as tetramethylsilane, trimethylsilane, trimethylisopropylsilane and trimethyl n-propylsilane, having a boiling point not higher than 100°C at 100 kPa absolute pressure.

Mixtures of blowing agents may be employed. The blowing agent is employed in an amount sufficient to enable the production of the foam. It is advantageous to use 3 to 18 percent by weight of blowing agent based on the polymer, preferably 4 to 15 percent.

Due to environmental concerns, it is preferred to employ blowing agents having an ozone depletion potential of zero or less. It is preferred to employ a partially or entirely pristine blowing agent. The term pristine blowing agent, as used herein, is meant to define nonhalogenated blowing agents such as, for example, carbon dioxide, nitrogen, water and argon. In one embodiment it is preferred to use carbon dioxide alone or in admixture with one



or more of the previously described blowing agents. In a particularly preferred embodiment, CO<sub>2</sub> is the only blowing agent. In a preferred embodiment of the invention; the blowing agent is a mixture of CO<sub>2</sub> and a lower alcohol of from 1 to 6 carbon atoms, more preferably up to 4 carbon atoms. Examples of lower alcohols include, for example, methanol, ethanol, 5 isopropanol, propanol, butanol, pentanol and hexanol, with ethanol being more preferred. In another preferred embodiment, the blowing agent is a mixture of CO<sub>2</sub> and a hydrocarbon blowing agent, with alkanes being preferred.

The blowing agent employed in the present invention preferably comprises 5 weight percent or more, preferably 10 weight percent or more, and more preferably 20 weight 10 percent or more carbon dioxide based upon the total weight of the blowing agent. It is advantageous to employ as much carbon dioxide as possible in the blowing agent while still making a desirable foam structure because carbon dioxide is economical and does not harm the environment.

Small amounts of water (0.1 to 4 weight percent) may be used in the foam 15 preparation process with or without an appropriate solubilizing or dispersing agent such as an alcohol, glycol or surfactant. In the preparation of foams in accordance with the method of the invention, it is often desirable to add a nucleating agent to the styrenic resin. These nucleating agents serve primarily to increase cell count and reduce the cell size in the foam and are used in an amount of 0.1 part by weight to 4 parts by weight per 100 parts resin. For example, talc, 20 sodium bicarbonate/citric acid and calcium silicate are suitable nucleating agents for reducing cell size. Talc is a preferred nucleating agent. Various other additives, for example, flame retardant additives, color concentrates, stabilizers, anti-oxidants or lubricants also may be used depending on the end use of the styrenic foam.

The invention comprises a method for producing a styrenic foam having a 25 thickness of from 0.04 to 4.0 inches or more, using the blowing agent compositions of the invention. Packaging foams are anywhere from 0.04 to 0.200 inches, while insulating foams may be as thick as 4.0 inches or higher. In the preferred method of the invention, a styrenic foam is produced from a "styrenic resin," which means a solid polymer of one or more polymerizable monovinyl aromatic compounds or a compatible mixture of such polymers.

30 In the method of the invention, the styrenic resin is mixed with a blowing agent composition and the resulting mixture is then foamed according to methods well-known to those skilled in the art. Preferably, the foaming is carried out with the use of an extruder, wherein the styrenic polymer is heated to a temperature of from 200 to 280°C to produce a molten polymer and the blowing agent is then introduced into the extruder where it is mixed 35 with the molten polymer under pressures such that the resulting plasticized extrusion mass does not foam, but its viscosity decreases. The extrusion mass is then cooled. Cooling increases the viscosity and the melt strength of the mass prior to extrusion. The mass is then extruded

through a die of any desirable shape of a controlled temperature, usually 100 to 150°C, the reduced pressure outside the extruder permitting the extrusion mass to foam.

In practicing the method of the invention, the blowing agent may be added to the styrenic resin in any desirable manner and preferably is added by injection of a stream of the blowing agent composition directly into the molten styrenic resin in the extruder. The blowing agent should be mixed thoroughly with the styrenic resin before the blowing agent and styrenic resin mass is extruded from the die. This is necessary to produce a foam having uniform density and cellular structure.

The extrusion mass comprising the molten resin and the blowing agent composition is extruded into an expansion zone within which foam formation and expansion takes place. Any suitable extrusion equipment capable of processing foamable styrenic compositions can be used for the extrusion. Single or multiple-screw extruders can be used. Softening the polymer and mixing with the blowing agent take place during working of the polymer between flights of the screw or screws, which also serve to convey the extrusion mass to the extruder die. Screw speed and extruder barrel temperature should be such as to achieve adequate mixing and softening but not so high as to degrade the composition being processed.

The foams can be used in the form prepared, cut into other shapes, further shaped by application of heat and pressure or otherwise machined or formed into shaped articles of desired size and shape.

The foam structure is preferably closed-cell, and has a closed-cell content of at least 90 percent according to ASTM D2856-87. The foam structure preferably has a density of 16 to 80 kilograms per cubic meter according to ASTM D-3575. The foam further preferably has an average cell size of 0.05 to 2.4 millimeters.

The following experiments illustrate the present invention and should not be construed to limit its scope. All parts and percentages are by weight and all temperatures are degrees Celsius unless otherwise indicated. The abbreviations used in the tables include Mw (weight average molecular weight), Mn (number average molecular weight), PAMS (polyalphamethylstyrene), SAMS (styrene alpha-methylstyrene copolymer) and Wt% (weight percent).

#### Example 1 - Polystyrene plus PAMS

Polymer formulations are prepared by dry blending a small quantity of plasticizer with a general purpose polystyrene resin. The polystyrene resin is a non-plasticized high molecular weight resin with an Mw of 320,000 a.m.u. and a polydispersity ratio (that is, the ratio Mw/Mn) of 2.4. The dry blend is then extruded to obtain a homogeneous blend. The extrudate is cut into small granules and all the testing is done on the formulation of these small granules.

Two poly(alpha-methylstyrene) polymers are employed as the plasticizer. The first is a low molecular weight homopolymer of alpha-methylstyrene, designated PAMS-A, which is commercially available from Amoco Chemical Company as Resin 18-240. It has an Mw of 6,700 and an Mn of 500. It contains approximately 20 percent volatile components as measured at 200°C for 100 minutes under a vacuum of 2 mm Hg. PAMS-A has a glass transition temperature of 122°C as measured by differential scanning calorimetry (DSC). The second polymer, PAMS-B, is commercially available from Amoco Chemical Company under the designation Resin 18-290. It is a homopolymer of alpha-methylstyrene with a glass-transition temperature of 142°C, an Mw of 11,900 and an Mn of 400. The total volatile content for PAMS-B is 14 percent.

As a comparative experiment the base non-plasticized polystyrene is blended with 2.5 percent white mineral oil.

Testing is done according to the following standard test procedures. The results of the testing are given in Table 1.

As used herein, the weight average molecular weight, Mw, and number average molecular weight, Mn, for the polymers are determined by the gel permeation chromatographic techniques described by ASTM test method D-3536 (polystyrene standard) and expressed without correction for the differences between polymers and polystyrene standards.

Vicat heat distortion temperature (HDT) is measured using injection molded test bars according to ASTM test method D1525-87, rate B, load 1 kg.

The melt flow rate (MFR) is measured using a Zwick MFR Measurement Apparatus according to the test procedure ASTM D-1238-86 at 200°C with a 5 kg load.

Flexural strength and flexural modulus are measured on injection molded bars prepared using an Arburg All Rounder 170 CMD injection molding machine. The following conditions are employed for the machine: the temperature profile is 210°C, 215°C, and 220°C; and the nozzle temperature is 225°C. The mold temperature is 30°C; the injection speed is 20 cm<sup>3</sup>/sec; and the injection pressure is 1,300 bar.

Flexural properties are determined using a Zwick Tester in 3-point bending mode according to the test procedure ASTM D-790.

Table 1  
Composition and Property Data for Pure and Plasticized Polystyrene  
versus PAMS-A and PAMS-B Modified Polystyrene

<u>Example</u>	<u>A1*</u>	<u>A2*</u>	<u>A3</u>	<u>A4</u>	<u>A5</u>	<u>A6</u>	<u>A7</u>	<u>A8</u>
% Mineral Oil	0	2.5	0	0	0	0	0	0
% PAMS-A	0	0	5	10	0	0	0	0
% PAMS-B	0	0	0	0	5	10	20	8
MFR (g/10 min.)	1.5	2.5	2.5	3.4	2.4	3.1	5.0	2.9
Vicat HDT (°C)	108.0	98.0	105.6	103	106.9	105.1	103.1	106
Flexural Str. (MPa)	93.4	86.0	95.9	97.7	97.1	98.9	87.1	95
Flex. Modulus (MPa)	3040	3000	3175	3150	3190	3190	3410	3200
Elongation (%)	3.3	3.4	3.4	3.5	3.5	3.6	2.8	3.5

\* Comparative experiment - not an embodiment of the invention

The data in Table 1 indicate that incorporation of PAMS-A and PAMS-B at levels between 5 percent and 20 percent results in a polymer that possesses improved properties. Incorporation of mineral oil into the polymer improves the melt flow rate but also causes a dramatic reduction in flexural strength and Vicat heat distortion temperature. The unplasticized base polymer has good flexural properties but its melt flow rate is low.

**Example 2 - Polystyrene plus Polyterpene**

The method of Example 1 is repeated with the following exceptions. Commercially available low molecular weight polyterpene resins are used as polymeric plasticizers. These resins are available from Yasuhara Chemical Co. Ltd. under the trade name CLEARON resins. The properties for blends of polystyrene and 10 percent CLEARON polyterpene resins, specifically CLEARON T0115 (T<sub>g</sub> = 63°C) nonhydrogenated and CLEARON M115 (T<sub>g</sub> = 61°C) semi-hydrogenated resins, are given in Table 2. The blank (Experiment B1) STYRON® 648 brand polystyrene, available from The Dow Chemical Company, is extruded twice in order to make it comparable with other blends.

Table 2  
Blends of STYRON® 648 and Polyterpene Resins

<u>Experiment</u>	<u>B1*</u>	<u>B2</u>	<u>B3</u>
Composition	STYRON® 648	10% CLEARON T0115	10% CLEARON M115
Appearance	Clear	Clear	Clear
MFR (g/10 min)	2.4	4.9	4.3
Vicat HDT (°C)	108.3	103.3	105.2
Flex. St. (MPa)	94	91	95
Flex. Mod. (MPa)	2880	2940	2930

\*Comparative experiment

As indicated by the results in Table 2, substantial improvement in flow is obtained without any significant drop in either heat distortion properties or in any flexural strength properties. All the blends are as transparent as polystyrene B1.

Example 3 - Polystyrene plus SAMS or PAMS

A low molecular weight copolymer of styrene and alpha-methylstyrene is made via free radical copolymerization of a mixture of styrene monomer and alpha methyl styrene monomer in a 1.5 liter batch reactor fitted with a jacket for heat exchange and a hollow shaft  
5 agitator with helical blades. The polymerization feed contains 60 percent alpha-methylstyrene monomer and 40 percent styrene monomer. The polymerization feed also contains 2000 ppm of the initiator 1,1'-bis(tert-butyl peroxy)cyclohexanone which is commercially available from Akzo Chemicals as TRIGONOX 22. The monomers are polymerized by increasing the temperature of the polymerization mixture from 130 to 190°C over a period  
10 of 9 hours at a heating rate of 15°C per hour. During the polymerization a chain transfer agent, n-dodecyl mercaptan, is added at a level of 2000 ppm four times. After 9 hours the conversion of the monomers reaches 65 percent solids and the resultant mixture is devolatilized in a vacuum oven at 230°C for 30 minutes applying full vacuum. The resulting polymer is called SAMS-A and has the following properties:

15

	Total residual monomers	6.2%
	Trimers	1.7%
	Mw	26,800
20	Mn	13,800
	Tg	115°C

Analysis by IR spectroscopy indicates that the polymer is 65.5 percent alpha-methylstyrene and 34.5 percent styrene. The properties of a series of styrene alpha-  
25 methylstyrene (SAMS) copolymers commercially obtained from Hercules Corporation under the trade name KRISTALEX are given in Table 3.

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Table 3  
Properties of KRISTALEX SAMS Copolymers

	<u>Designation</u>	<u>SAMS-B</u>	<u>SAMS-C</u>	<u>SAMS-D</u>	<u>SAMS-E</u>	<u>SAMS-F</u>
5	Commercial designation	F85	F100	1120	3085	5140
	Wt% AMS	44	48	60	47	41
	Mw	1610	2000	2075	1860	6100
	Mn	1360	1590	691	1580	3550
10	Volatiles(%)	15.8	8.4	17.4	12.7	4.2
	Tg (°C)	83	81	111	88	121

Blends of these resins and a high flow polystyrene resin XZ86609.02, (hereinafter referred to as Resin XZ) which is available from The Dow Chemical Company, are made according to the method of Example 1 and the properties are given in Table 4.

Table 4  
Properties of Blends of Polystyrene Resin XZ and SAMS Copolymers

	<u>Experiment</u>	<u>C1*</u>	<u>C2</u>	<u>C3</u>
20	Composition	Resin XZ	15% SAMS-A	10% SAMS-D
	MFR (g/10 min)	8.7	15	15
	Vicat SP (°C)	108	104	104
25	Flex. Str. (MPa)	75	75	69
	Flex. Mod. (MPa)	2950	3090	3210
	Flex. Elongation (%)	2.6	2.4	2.1

\*Comparative experiment

Similarly, blends of Resin XZ and a series of SAMS and PAMS materials are prepared. The physical properties of these blends are given in Table 5.

Table 5

Blends of SAMS and PAMS Plasticizers with Polystyrene Resin XZ

	<u>Experiment</u>	<u>D1*</u>	<u>D2</u>	<u>D3</u>	<u>D4</u>	<u>D5</u>
5	Composition	Resin XZ	10% PAMS-A	10% PAMS-B	10% SAMS-D	16% SAMS-D
	MFR (g/10 min)	9.7	17.3	16.4	18	29
	Vicat (°C)	107	100	102	103	102
	Fl.St. (MPa)	72	65	65	66	55
10	Fl. Mod (MPa)	3140	3160	3140	3140	3240
	Fl. Elong (%)	2.3	1.9	2.0	2.0	1.6

\* Comparative experiment

15 Table 6 summarizes a series of experiments wherein the level of PAMS is varied to determine the effect on flow and Vicat HDT.

Table 6

Flow and Heat Distortion Properties  
of PAMS/Polystyrene Blends

	<u>Blend Ratio PAMS</u>	<u>Vicat SP (°C)</u>	<u>MFR (g/10 min.)</u>
20	100% Resin XZ	108	7.3
	97% Resin XZ + 3% PAMS-B	107	9.4
	93% Resin XZ + 7% PAMS-B	106	10.1
	90% Resin XZ + 10% PAMS-B	105	11.8
25	87% Resin XZ + 13% PAMS-B	104	13.3
	85% Resin XZ + 15% PAMS-B	103	17

30 All of the plasticizer copolymers and homopolymers tested have higher glass-transition temperatures than that of the base polystyrene. Despite the higher T<sub>g</sub>, a higher than expected drop in the Vicat HDT of the blends is sometimes observed. It is believed that this reduction in the heat properties is due to the fact that all the plasticizer polymers contain some volatiles. These volatiles cause a drop in the heat properties when mixed with the polystyrene matrix. In order to demonstrate this point, two SAMS copolymers are made

35 containing less than 1 percent of volatile components. These two SAMS copolymers are prepared by anionic polymerization in hexane using n-butyl lithium as the initiator. The resulting polymers have the properties listed in Table 7.



Table 7  
Properties of Anionically Polymerized SAMS Copolymers

	<u>Designation</u>	<u>SAMS-G</u>	<u>SAMS-H</u>
5	Composition % AMS	63	62
	Composition % styrene	37	38
	Mw	7700	9500
	Mw/Mn	1.08	1.08
10	% Volatiles	0.67	0.50
	Tg (°C)	125	130

SAMS-G and SAMS-H are compounded with STYRON® 648 by extrusion blending.

15 The blend properties are listed in Table 8.

Table 8  
Properties of Blends of STYRON® 648 and Anionically  
Polymerized SAMS Copolymers and Polystyrene

	<u>Experiment</u>	<u>E1*</u>	<u>E2</u>	<u>E3</u>
20	Composition	STYRON 648	10% SAMS-G	10% SAMS-H
	MFR (g/10 min.)	2.01	2.80	2.84
	Vicat HDT (°C)	108.6	110.6	111.1
	Flex ST (MPa)	89	90	89
	Flex. Mod (MPa)	3100	3155	3175
25	Flex Elong. %	3.0	3.0	2.9

\*Comparative experiment

The results in Table 8 indicate that the heat distortion temperature of the blends increases in the absence of high levels of volatile components.

30 Table 9 gives the property balance of blends of SAMS-(B through F) with STYRON® 648.

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Table 9  
Properties of Commercially Available SAMS Copolymers and Their  
Blends with STYRON® 648 brand Polystyrene

	Exp. No.	Blend Compn.	MRF (g/10 min.)	Vicat SP (°C)	Flex St. (MPa)	Flex Mod. (MPa)	Flex Elong. (%)
5	F1*	STYRON 648	2.2	108.7	99	3120	4.4
	F2	5% SAMS-B	3.1	104.8	95	3155	3.9
	F3	10% SAMS-B	4.3	101.3	93	3140	4.2
	F4	5% SAMS-C	2.9	106.2	96	3145	3.9
10	F5	10% SAMS-C	4.4	103.2	94	3145	4.1
	F6	5% SAMS-D	3.3	107	89	3110	3.1
	F7	10% SAMS-D	4.3	105.6	94	3165	3.9
	F8	5% SAMS-E	2.8	105.6	93	3110	3.1
15	F9	10% SAMS-E	5.3	101.7	94	3165	4.2
	F10	5% SAMS-F	2.3	108.3	98	3130	4.1
	F11	10% SAMS-F	3.0	107.6	97	3203	4.1

\* Comparative example.

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All the examples of the invention show clearly that the blends of the polymeric plasticizers with polystyrene resins result in the improvement of the flow properties and cause no reduction or minimal reduction in the heat distortion properties and physical properties.

Example 4 - HIPS plus PAMS

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Blends of PAMS-A and -B with a high impact polystyrene (HIPS) commercially available from The Dow Chemical Company under the designation STYRON® 472 are prepared using the method of Example 1. STYRON® 472 is a mass polymerized HIPS containing 8.5 percent rubber of 3.5 micron average particle size. The physical properties of the blends are summarized in Table 10.

30

The following additional test procedures are employed.  
Tensile: ASTM D 638-87B at 5 mm/min.  
Izod impact: ASTM D256-87.  
Charpy impact: ISO 179-2C.

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Table 10  
Blending PAMS-A and PAMS-B with HIPS

	<u>Experiment</u>	<u>G1*</u>	<u>G2</u>	<u>G3</u>	<u>G4</u>	<u>G5</u>
5	% PAMS-A	0	5	10	0	0
	% PAMS-B	0	0	0	5	10
	MFR (g/10 min.)	3.6	5.1	7.0	4.7	5.7
	Vicat (°C)	101.5	99.3	96.5	99.8	98.1
10	Izod Im. (J/M)	112	105	87	106	89
	Charpy (kJ/M <sup>2</sup> )	8.4	7.6	6.4	7.5	6.5
	Ten. Yield. (MPa)	16.5	16.6	16.9	17.1	17.5
	Ten. Rup. (MPa)	19.5	19.6	19.3	20.3	19.6
15	Elong. (%)	55	54	49	55	46
	E-mod. (MPa)	1515	1565	1610	1620	1660

\* Comparative experiment - not an embodiment of the invention

20 Table 10 again clearly demonstrates the benefits of using PAMS materials of the invention to obtain improved flow properties. The tensile properties are generally improved. The impact reduction in Experiments G2-G5 compared to G1 is a result of the reduced, percentage-wise, polybutadiene content due to incorporation of the PAMS materials. The clear improvement in modulus and melt flow rate is highly desirable and surprising, as current  
25 plasticizers are not capable of improving both of the properties.

#### Example 5 - Foam

##### Example 5A

Closed-cell styrene polymer foams are prepared utilizing a 2-inch diameter extruder which feeds a mixer. The mixer discharge stream is passed through 3 heat exchangers.  
30 The discharge from the heat exchangers is passed through a static mixer, and is expanded through a slot die into a region of lower pressure.

A mixture of a polystyrene resin having a weight average molecular weight of 200,000 as measured by liquid chromatography and PAMS-B is prepared according to the method of Example 1 and is fed to the extruder with 2.5 pph (parts per hundred based on  
35 polymer) of hexabromocyclododecane (HBCD), 0.2 pph of tetrasodiumpyrophosphate (TSPP) 0.2 pph of barium stearate and 0.15 pph of a cyano-phthalo blue dye concentrate. PAMS-B is added at levels of 1 and 2.9 percent based on the weight of the total polymer mixture. Blowing agents are injected into the mixer in the amounts identified in Table 11. The foamable gel is

cooled to 129°C and extruded through the die and expanded between substantially parallel forming plates. Foam production conditions and physical property values of the resulting foams are given in Table 11.

Table 11

5	Exp. No.	Poly- styrene	<u>Blowing Agent</u>		
			PAMS-B	Additives	HCFC-142b    CO <sub>2</sub>
		%	%	(pph)	(pph)    (pph)
	H1*	100	0	3.05	10    2
10	H2	99	1	3.05	10    2
	H3	97.1	2.9	3.05	10    2
15	<u>Pressure</u>				
		Mixer	Die	Pressure Drop	Density    Cell Size
		(bar)	(bar)	(bar)	(kg/m <sup>3</sup> )    (mm)
	H1*	143	63	80	36.7    0.20
	H2	132	59	73	35.0    0.23
	H3	133	65	68	33.0    0.25
20	<u>Compressive strength</u>				
		Vertical	Extrusion	Horizontal	HDT    WD
		(kPa)	(kPa)	(kPa)	(°C)    (%)
	H1*	534	229	247	73    3.10
25	H2	489	228	239	76    1.91
	H3	466	197	231	73    2.09

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## E.D.C.

	Vertic.	Extrusion	Horiz.	Vol.	Skin	
	(%)	(%)	(%)	(%)		
5	H1*	0	5.6	0.6	6.2	Good
	H2	0.3	4.9	1.1	6.3	Good
	H3	0.2	6.6	0.7	7.5	Accept- able

\* Comparative Experiment

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Surprisingly, the foam density for Experiments H2 and H3 is lower than that of H1, the control. The compressive strength values are equivalent to that of the control foam at equivalent foam density. The heat resistance performance as measured by the "WD" test (German DIN-18164 standard), and the heat distortion temperature is maintained or improved.

5    Example 5B

Foams are produced using the procedure and apparatus of Example 5A with the following exceptions. The blowing agent is a mixture of 3 pph carbon dioxide and 3.5 pph ethanol. The PAMS-B level ranges from 2.9percent to 9.1percent total of the polymer mixture. Foam production conditions and physical properties are given in Table 12.

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Table 12

Exp. No.	Poly-styrene	PAMS-B	Additives	Blowing Agent		
				Ethanol	CO <sub>2</sub>	
5	(%)	(%)	(pph)	(pph)	(pph)	
	I4*	100	0	2.15	3.5	3
	I5	97.1	2.9	2.15	3.5	3
	I6	95.2	4.8	2.55	3.5	3
10	I7	90.9	9.1	2.55	3.5	3

		Pressure		Pressure Drop	Density	Cell Size
		Mixer	Die			
		(bar)	(bar)	(bar)	(kg/m <sup>3</sup> )	(mm)
15	I4*	168	68	100	36.2	0.38
	I5	150	65	85	34.6	0.34
	I6	146	56	90	35.0	0.43
	I7	138	61	77	34.2	0.40

		Compressive strength			HDT	WD
		Vertic.	Extrusion	Horiz.		
		(kPa)	(kPa)	(kPa)	(°C)	(%)
	I4*	446	176	240	88	1.40
25	I5	382	193	245	88	2.27
	I6	406	232	227	91	2.27
	I7	408	198	222	88	2.03

		E.D.C.			Skin	
		Vertic.	Extrusion	Horiz.		
30		(%)	(%)	(%)	(%)	
	I4*	-0.2	0.9	-0.3	0.4	Good
	I5	-0.2	-0.3	0.6	0.1	Acceptable
	I6	-0.2	0.0	0.0	-0.2	Good
35	I7	-0.1	0.7	-0.2	0.4	Good

\* Comparative Experiment

Example 5B demonstrates the lower foam density, reduced pressure drop and good mechanical properties, including dimensional stability, obtained using the invention.

#### Example 5C

- The procedure of Example 5A is followed with the following exceptions. The apparatus is a 1 1/4 inch screw-type extrusion line with a slit die. The temperature of the cooling zone is adjusted so that the gel is cooled to a uniform temperature of 135°C to 140°C. Further details and results are contained in Table 13.

Table 13

Exp. No.	Poly-styrene (%)	PAMS-B (%)	Blowing Agent		
			CO <sub>2</sub> (pph)	H <sub>2</sub> O (pph)	
J8*	100	0	4.5	0	
J9	80	20	4.0	0	
J10*	100	0	4.0	0.3	
J11	80	20	4.0	0.3	

  

	Pressure		Pressure Drop (bar)	Density (kg/m <sup>3</sup> )	Cell Size (mm)	Skin
	Mixer (in bar)	Die (bar)				
J8*	227	128	99	39.6	0.21	Good
J9	189	119	70	40.4	0.26	Good
J10*	207	121	86	38.5	0.21	Good
J11	177	110	67	36.7	0.35	Good

\* Comparative Experiment

The results of Example 5C confirm the effect of the invention using different blowing agents, including CO<sub>2</sub> alone and CO<sub>2</sub> with water.

#### 30 Foam Physical Property Testing Methods

Density: ASTM D-1622.

Cell size: ASTM D 3576-77.

Compressive Strength: ASTM 1621-79.

WD test: German DIN 18164.

- Heat distortion temperatures (HDT) are measured according to the following test method. The average value of three specimens is reported. Extruded foam is cut into sample blocks 20 cm long and 10 cm wide, with the thickness as extruded. A block is placed in an oven, heated to a specified temperature, held at that temperature for 1 hour, and then is allowed to



cool to ambient temperature. Testing conditions start at 73°C. Foam dimensions are measured before heating and after cooling. The test is then repeated with new samples, increasing the temperature in increments of 3°C for each new sample, and this is repeated until the specimens fail. Failure is determined by a volume change of more than 5percent or a change in length, width or height of more than 2percent. The reported value is the last non-failing value.

5 Environmental dimensional change (E.D.C.): ASTM C-578-83.

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1. An optionally rubber-reinforced monovinylidene aromatic polymer composition comprising:
  - (a) an optionally rubber-reinforced monovinylidene aromatic polymer; and having a weight average molecular weight of at least about 100,000; and
  - 5 (b) a plasticizing amount of a low molecular weight polymer of limonene or alpha-methylstyrene having a weight average molecular weight of from 1,000 to 70,000, a volatiles content of up to 30percent and a glass transition temperature of at least 25°C.
2. The composition of Claim 1 wherein the polymer of (b) is a homopolymer  
10 of limonene.
3. The composition of Claim 1 wherein the monomer of the low molecular weight polymer is alpha-methylstyrene.
4. The composition of Claim 1 wherein the polymer of (b) is a copolymer of styrene and alpha-methylstyrene.
- 15 5. The composition of Claim 1 wherein component (a) is at least 70percent by weight of the composition.
6. The composition of Claim 1 which is substantially free of polyphenylene oxide.
7. The composition of Claim 1 wherein the  $T_g$  of the polymer of (b) is at least  
20 50°C.
8. The composition of Claim 7 wherein the  $T_g$  of the polymer of (b) is at least 70°C.
9. A monovinylidene aromatic polymer composition consisting essentially of an optionally rubber-reinforced monovinylidene aromatic polymer having a weight average  
25 molecular weight of at least 100,000 and a plasticizing amount of a polymer of limonene or alpha-methylstyrene having a weight average molecular weight of from 1,000 to 70,000, a volatiles content of up to 30percent and a glass transition temperature of at least 25°C.
10. A process for producing a closed-cell polymer foam comprising heating the composition of Claim 1 to a temperature sufficient to provide a molten polymer; admixing a  
30 blowing agent with said molten polymer to provide a plasticized mixture; heating the mixture to a temperature and applying a pressure such that the plasticized mixture does not foam; thereafter, reducing the temperature of the mixture to increase its viscosity; and extruding the plasticized mixture into a zone at a temperature and pressure sufficient to permit foaming.
11. An expandable monovinylidene aromatic polymer formulation comprising:  
35 (A) a monovinylidene aromatic polymer having a weight average molecular weight of at least 100,000;

(B) a low molecular weight polymer of limonene or alpha-methylstyrene having a weight average molecular weight of from 1,000 to 70,000, a volatiles content of up to 30percent and a glass transition temperature of at least 25°C; and  
(C) a blowing agent.

5                   12. The formulation of Claim 11 wherein the monovinylidene aromatic polymer is polystyrene.

                  13. The formulation of Claim 12 wherein the low molecular weight polymer is poly(alpha-methylstyrene).

                  14. The formulation of Claim 12 wherein the limonene comprises d-limonene.

10                  15. The formulation of Claim 12 wherein the blowing agent comprises CO<sub>2</sub>.

                  16. The formulation of Claim 12 wherein the blowing agent consists essentially of CO<sub>2</sub>.

                  17. A polymer foam comprising:

                  (A) a monovinylidene aromatic polymer having a weight average molecular weight of at least  
15   100,000; and

                  (B) a low molecular weight polymer of a vinyl aromatic monomer or limonene having a weight average molecular weight of from 1,000 to 70,000, a volatiles content of up to 30percent and a glass transition temperature of at least 25°C.

                  18. The foam of Claim 17 wherein the low molecular weight polymer is  
20   poly(alpha-methylstyrene).

                  19. The foam of Claim 17 wherein the limonene comprises d-limonene.

                  20. The foam of Claim 17 wherein the low molecular weight polymer is a copolymer of styrene and alpha-methylstyrene.

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# INTERNATIONAL SEARCH REPORT

Int ional Application No  
PCT/US 94/06112

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C08L25/02 C08J9/12 //(C08L25/02, C08L25:16), (C08L25/02, C08L47:00)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C08L C08J C08F C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CHEMICAL ABSTRACTS, vol. 80, no. 6, 11 February 1974, Columbus, Ohio, US; abstract no. 27913, 'photodegradable resin compositions' page 35 ; see abstract & JP,A,48 064 135 (SEKISUI CHEM CO LTD) 5 September 1973	1,2,5,6, 9
Y	US,A,4 959 412 (ARTER ET AL) 25 September 1990 see claims 1,6; table 1	1,2,5,6, 9
X	BE,A,633 239 (DOW CHEM. COMP.) see claims 1,8-12; table II	1,3,5-9
	--- -/-- ---	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- \* & \* document member of the same patent family

Date of the actual completion of the international search

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Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

Int ional Application No  
PCT/US 94/06112

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB,A,2 043 648 (JAPAN STYRENE PAPER CORP.) 8 October 1980 see page 2, line 45 - line 53	1,3,6-9
X	see claims 1,3 -----	11-13

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/06112

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US-A-4959412	25-09-90	NONE	
BE-A-633239		DE-B- 1265406 FR-A- 1366197 GB-A- 1036448 NL-A- 293626 US-A- 3303159	
GB-A-2043648	08-10-80	JP-C- 1280623 JP-A- 55118932 JP-B- 58035614 BE-A- 882120 CA-A- 1143118 DE-A, C 2923610 FR-A, B 2450685 SE-B- 442207 SE-A- 8001806 US-A- 4260572	13-09-85 12-09-80 03-08-83 08-09-80 22-03-83 11-09-80 03-10-80 09-12-85 10-09-80 07-04-81